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3D Nanoscale Analysis of Zeolite Catalysts by Electron Tomography and Image Processing

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For more than a decade now, electron tomography (ET), also known as 3D-TEM (transmission electron microscopy), has continuously proven to be an important tool in the field of materials science [1]. Conventional TEM is limited by detection difficulties caused by overlapping features in 2D projections i.e. TEM micrographs. ET overcomes this limitation and provides information also in the third dimension, yielding 3D reconstructions which provide an insight into the internal structure of the particle. When combined with image analysis, ET becomes a powerful quantitative tool, capable of measuring properties at the nanometer scale which are inaccessible to commonly used characterization techniques. In this paper we describe the methodology of combining ET and advanced image analysis that led to unraveling some of the important properties of industrially applied zeolite catalysts which were never accessed before.

The study focuses on mesoporous (2-50 nm diameter pores) zeolite Y, before and after Pt nanoparticles were deposited on it. This is an important catalyst used in oil refineries. Its catalytic performance depends greatly on the number of morphological properties, including connectivity and accessibility of the mesopores (diffusion of the molecules to the zeolite active acid sites) and the accessibility of the Pt nanoparticles (active metal sites) whose size and distribution within the zeolite might vary with preparation methods. To image the internal structure of zeolite catalysts, we performed ET using a Tecnai 20 transmission electron microscope (FEI) and IMOD software for obtaining 3D reconstructed volumes of zeolite particles. The resolution of the 3D reconstructions was in order of 1-3 nm, which allowed detection of both mesopores and, if present, Pt nanoparticles. To extract quantitative data, reconstructed volumes were submitted to a number of image processing steps using SDC or DipLib toolbox in Matlab. Firstly, the 3D reconstructions were filtered using median or alternating sequential filters to reduce the noise (Fig. 1a). Filtered volumes were then thresholded to obtain binary volumes (Fig. 1b) using different grey values depending on which feature of the particle (mesopores or Pt) is of interest. Once isolated, i.e. segmented, mesopores (Fig. 1c) or Pt particles were then submitted to advanced image processing operations yielding quantitative information.

In case of analyzing the mesopores [2], image processing operation called geodesic reconstruction of binary volumes allowed us to distinguish open mesopores - accessible from the surface of the crystal (Fig. 2a), from closed mesopores which are only accessible through micropores and believed to have hardly any influence on enhancing diffusion through a zeolite crystal (Fig. 2b). Furthermore, the shape of the mesopores was quantitatively characterized through a tortuosity factor (~1.3), which compares the Euclidean and geodesic distances from any point of the mesopore space to the outer surface of the grain. The size (and the size distribution) of the microporous (< 2 nm pores) zeolite regions, crucial for understanding the diffusion of smaller molecules to the active acid sites within the zeolite, was also determined by Euclidean distance transform (Fig. 2c).

Optimal experimental conditions enabled for the first time high-resolution 3D imaging of Pt particles as small as 1 nm located inside zeolite micropores (Fig. 2d). Using image analysis, diameters and volumes of the thousands of Pt nanoparticles, as well as the distances between nanoparticles, were determined. Such automated analysis allowed for many more Pt/zeolite crystals to be analysed, which led to discovery of great heterogeneities in loading of individual zeolite crystals within the same sample [3].

This study reveals the benefits of combining ET with advanced image processing operations for nanoscale analysis of complex morphological systems. The nanoscale features, such as open/closed mesopores or variation in Pt loading between crystals, can be very important for a macroscale catalyst performance and their determination and analysis is essential for catalyst design.

References:

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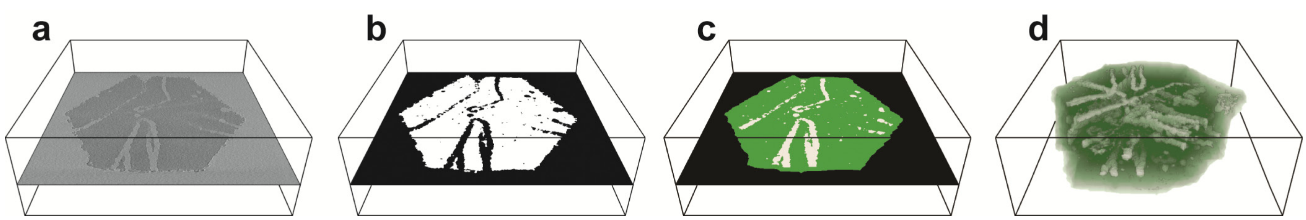

Figure 1. Image processing steps for obtaining segmented volumes of mesopores, including: filtering (a), binarizing (b), segmenting (c) and final visualization (d) of zeolite and mesopores within it.

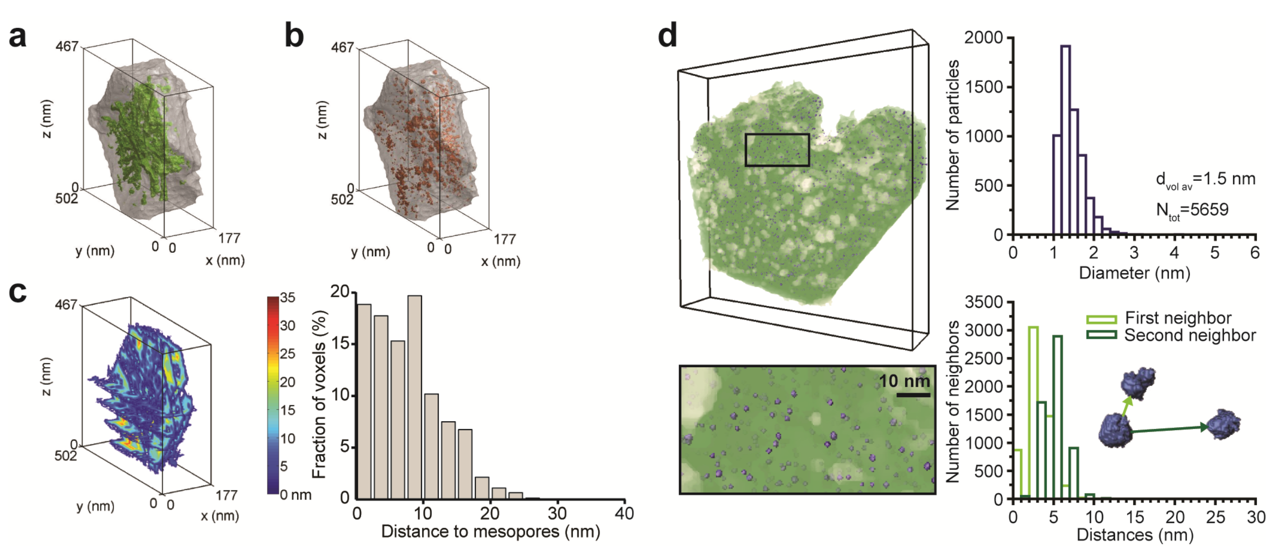

Figure 2. Quantitative image analysis of mesoporous and microporous regions of zeolite showing open (a) and closed (b) mesopores and size distribution of microporous regions (c). Analysis of Pt nanoparticles within the Pt/zeolite sample (d), yields the size and distance distribution of Pt particles. Adapted with permission from references [2, 3].

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